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Hidden Symmetries and Their Consequences in t_{2g} Cubic Perovskites

Abstract

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Disciplines

Physics

Comments

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Hidden symmetries and their consequences in t_{2g} cubic perovskites

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The five-band Hubbard model for a d band with one electron per site is a model which has very interesting properties when the relevant ions are located at sites with high (e.g., cubic) symmetry. In that case, if the crystal-field splitting is large, one may consider excitations confined to the lowest threefold-degenerate t_{2g} orbital states. When the electron hopping matrix element (t) is much smaller than the on-site Coulomb interaction energy (U), the Hubbard model can be mapped onto the well-known effective Hamiltonian (at order t^2/U) derived by Kugel and Khomskii (KK). Recently we have shown that the KK Hamiltonian does not support long-range spin order at any nonzero temperature due to several novel hidden symmetries that it possesses. Here we extend our theory to show that these symmetries also apply to the underlying three-band Hubbard model. Using these symmetries we develop a rigorous Mermin-Wagner construction, which shows that the three-band Hubbard model does not support spontaneous long-range spin order at any nonzero temperature and at any order in t/U —despite the three-dimensional lattice structure. The introduction of spin-orbit coupling does allow spin ordering, but even then the excitation spectrum is gapless due to a subtle continuous symmetry. Finally we show that these hidden symmetries dramatically simplify the numerical exact diagonalization studies of finite clusters.

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I. INTRODUCTION

The transition-metal oxides have been the source of many fascinating physical phenomena such as high-temperature superconductivity,¹ colossal magnetoresistance,² half-metallic perovskites,³ and orbiton physics.^{4–6} These surprising and diverse physical properties arise from strong correlation effects in the $3d$ bands. As a first step towards a better understanding of these systems, there is much recent interest in the magnetic properties of transition-metal oxides with cubic ABO_3 structure, where three d orbitals are degenerate^{4,5} (see inset to Fig. 1). In cubic oxide perovskites, the crystal field of the surrounding oxygen octahedra splits the d orbitals into a twofold-degenerate e_g and a threefold-degenerate t_{2g} manifold. In most cases, these degeneracies are further lifted by a cooperative Jahn-Teller (JT) distortion⁴ and the low-energy physics is well described by an effective superexchange spin-only model.^{7–9} However, some cubic perovskites, such as LaTiO_3 , do not undergo a significant JT distortion, in spite of the orbital degeneracy.¹² We will mainly consider the simplest “idealized” version of this model, in which the magnetic ions occupy sites whose local site symmetry is at least tetragonal. In these systems, the effective superexchange model must deal with not only the spin degrees of freedom but also the degenerate orbital degrees of freedom.^{4,5,13} The large degeneracy of the resulting ground states may then yield rich phase diagrams, with exotic types of order, involving a strong interplay between the spin and orbital sectors.^{5,10,11}

In the titanates, there is one d electron in the t_{2g} degenerate manifold, which contains the wave functions $|x\rangle \equiv d_{yz}$, $|y\rangle \equiv d_{xz}$, and $|z\rangle \equiv d_{xy}$. We will refer to $|x\rangle$, $|y\rangle$, and $|z\rangle$ as “flavors.” Following Kugel and Khomskii (KK),¹³ one

starts from a Hubbard model with on-site Coulomb energy U and nearest-neighbor (NN) hopping energy t . For large U , this model can be reduced to an effective superexchange model, which involves only NN spin and orbital coupling, with energies of order $\epsilon = t^2/U$. This low-energy model has been the basis for theoretical studies of the titanates.^{6,13–15} In particular, it has been suggested¹⁴ that the KK Hamiltonian gives rise to an ordered isotropic spin phase and that an energy gap in the spin excitations can be caused by spin-orbit interactions.¹⁵ However, these papers are based on assumptions and approximations which are hard to assess.

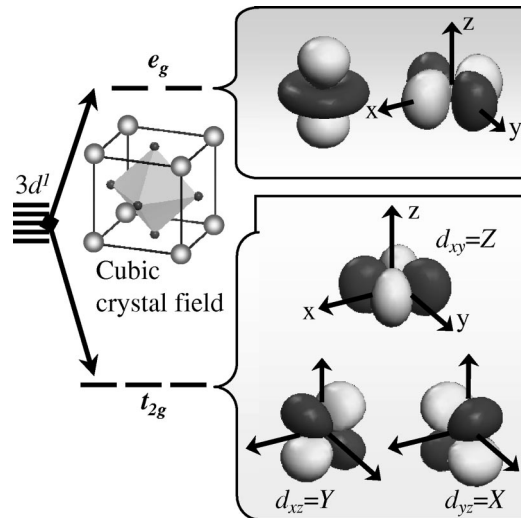


FIG. 1. A schematic view of the splitting of the fivefold orbitals under cubic crystal field. The transition metal is located at the center of the oxygen octahedron.

Recently¹⁶ (this will be referred to as I) we have presented rigorous arguments which show several unusual symmetries of the KK Hamiltonian. Perhaps the most striking symmetry is the rotational invariance of the total spin of the electrons in α -flavor orbitals in each plane perpendicular to the α axis. As reported previously in I, this symmetry implies that the system does not support long-range spin order at any non-zero temperature, *despite the underlying three-dimensional lattice structure*. Inclusion of a spin-orbit interaction destroys the independent rotational invariance of the spin associated with each orbital. Although long-range order at nonzero temperature occurs when this perturbation is included, the spin system still possesses enough symmetry that the excitation spectrum remains gapless.^{8,9,17} (This conclusion might be surprising, because once spin-orbit interactions are included, the system is expected to distinguish directions relative to those defined by the lattice.) The purpose of the present paper is to extend the theory for the KK model presented in I to the underlying three-band t_{2g} Hubbard model and to elaborate further on the consequences of these results.

Briefly this paper is organized as follows. In Sec. II we introduce the Hubbard model, which forms the starting point for “idealized” treatments of these systems, and we discuss the KK Hamiltonian which is its by-product. In Sec. III we derive the symmetry results both on the original Hubbard model and also on the KK Hamiltonian, which are central to most of our arguments. In Sec. IV we give the details of the Mermin-Wagner construction, which enables us to rigorously conclude that this model does not support long-range order. In Sec. V we show how these unusual symmetries lead to a dramatic simplification in the numerical determination of the ground state of a cube of eight sites governed by the KK Hamiltonian. In Sec. VI we give a symmetry analysis which shows that even in the presence of spin-orbit interactions the excitation spectrum must have a gapless Goldstone mode. In Sec. VII we summarize our work. Our major conclusion is that to understand real physical systems, such as LaTiO_3 , which do show long-range spin order and which do have a gap in their elementary excitation spectrum, it is crucial to include perturbations which destroy the symmetries described here.

II. HAMILTONIAN

The system we treat is a simple cubic lattice of ions with one electron per ion in a d band. Following the seminal work of Kugel and Khomskii,¹³ we describe this system by a Hubbard Hamiltonian \mathcal{H}_H of the form

$$\mathcal{H}_H = \sum_{i\alpha} \tilde{\epsilon}_\alpha N_\alpha(i) + \sum_{ij} \sum_{\alpha\beta\sigma} t_{\alpha\beta}(i,j) c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} + \frac{1}{2} \sum_i \sum_{\alpha\beta} U_{\alpha\beta} N_\alpha(i) N_\beta(i), \quad (1)$$

where $c_{i\alpha\sigma}^\dagger$ creates an electron in the orbital labeled α in spin state σ on site i and $N_\alpha(i) = \sum_\sigma c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma}$, $\tilde{\epsilon}_\alpha \equiv \epsilon_\alpha - (U_{\alpha\alpha}/2)$, where ϵ_α is the crystal field energy of the α orbital and $t_{\alpha\beta}(i,j)$ (which we assume to be real) is the

matrix element for hopping between orbital α of site i and orbital β of site j . Note that $t_{\alpha\beta}$ is zero if either $\alpha \neq \beta$ or if $\alpha = \beta$ is the inactive axis and otherwise it assumes the value t . Here we also have generalized the model so that instead of a single Coulomb energy U , we now introduce $U_{\alpha\beta}$, the direct Coulomb interaction between electrons in orbitals α and β on the same site. Note that this Hamiltonian does not include the somewhat smaller Coulomb exchange terms.^{18,19} [We write \mathcal{H}_H in the above form to emphasize that apart from the hopping term, the Hamiltonian is a function of $N_\alpha(i)$.] We assume that the crystal field splits the five orbital d states into three low-energy t_{2g} states, $d_{yz} \equiv |x\rangle$, $d_{xz} \equiv |y\rangle$, and $d_{xy} \equiv |z\rangle$, and that the two other e_g states have high enough energy that we can neglect their presence (Fig. 1). This structure is consistent with tetragonal or higher site symmetry. (For strictly cubic site symmetry the higher two states form a degenerate doublet and the lower three states a degenerate triplet. For lower-than-cubic symmetry the degeneracy in energy of the states is removed but, as long as the symmetry is tetragonal or higher, the wave functions are those listed.) We confine our attention to the wide class of materials in which hopping between magnetic ions is mediated by intervening oxygen ions. In that case, following KK, we note that the hopping matrix $t_{\alpha\beta}$ between NN's is diagonal in orbital indices and also $t_{\alpha\alpha} = 0$ if the NN bond lies along the α axis, which has been called¹⁸ the “inactive” axis for α hopping. Later on we will discuss modifications caused by farther-than-nearest-neighbor hopping via oxygen ions. The symmetry of the NN hopping matrix is illustrated in Fig. 2. Note that these symmetries only hold for tetragonal or cubic site symmetry. They are broken by a rotation of the oxygen octahedra.

When $t \ll U$, KK reduced the above Hubbard Hamiltonian at lowest order in t/U to an effective Hamiltonian for the manifold of states which remain when $U \rightarrow \infty$. We will call this Hamiltonian the KK Hamiltonian, and it will be denoted \mathcal{H}_{KK} . This Hamiltonian can be regarded as a many-band generalization of the Heisenberg Hamiltonian, which is obtained from the single-band Hubbard model with one electron per site, for which the exchange constant is $J = 4t^2/U$. To make the analogy with the Heisenberg model more apparent, the KK Hamiltonian is often written in terms of spin variables as

$$\mathcal{H}_{KK} = \epsilon \sum_{\langle ij \rangle} J_{ij} [1 + \mathbf{S}_i \cdot \mathbf{S}_j], \quad (2)$$

where $\mathbf{S}_i \equiv \frac{1}{2} \boldsymbol{\sigma}_i$ is the vector spin operator for an electron on site i , $\langle ij \rangle$ indicates that the sum is over pairs of nearest-neighbor ions, $\epsilon = t^2/U$, and the exchange “constant” is now an orbital operator written in terms of spinless fermion operators as

$$J_{ij} = \sum_{\alpha \neq ij} \sum_{\beta \neq ij} a_{i\alpha}^\dagger a_{i\beta} a_{j\beta}^\dagger a_{j\alpha}, \quad (3)$$

where $a_{i\alpha}^\dagger$ creates an electron in orbital $|\alpha\rangle$ on site i (of either spin) and $\alpha \neq ij$ means that we sum α over the values x, y ,

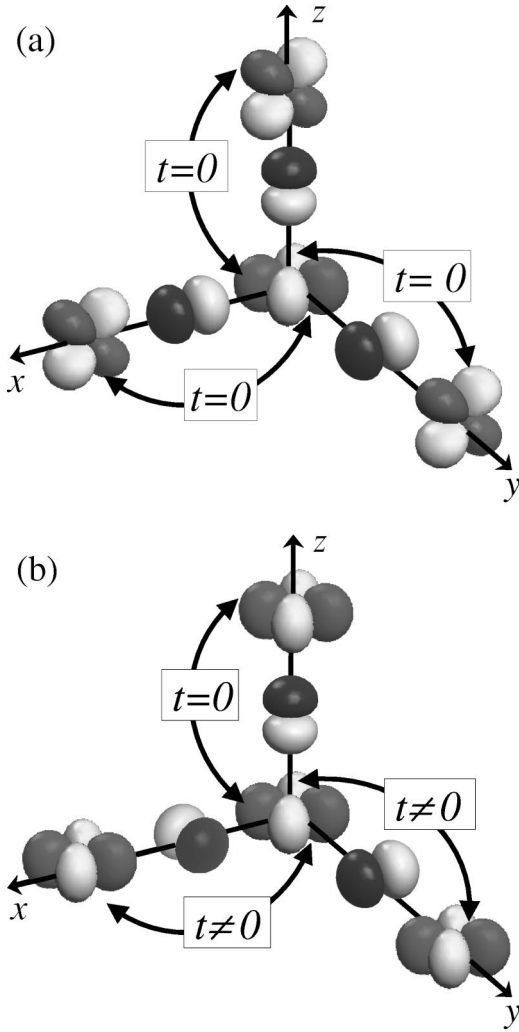


FIG. 2. Symmetry of the hopping matrix element for cubic site symmetry. (a) The hopping matrix between different flavors is zero. (b) The z axis is inactive for z orbitals.

and z , except for the value of α which corresponds to the coordinate direction of the bond ij , which is the inactive axis for orbital α .

For our purposes it is more convenient to write $\mathcal{H}_{\text{KK}} = \mathcal{H}_x + \mathcal{H}_y + \mathcal{H}_z$, where

$$\mathcal{H}_\alpha = \epsilon \sum_{\langle ij \rangle \in \alpha} \sum_{\beta, \gamma \neq \alpha} \sum_{\sigma, \eta} c_{i\beta\sigma}^\dagger c_{i\gamma\eta} c_{j\gamma\eta}^\dagger c_{j\beta\sigma}, \quad (4)$$

where $\langle ij \rangle \in \alpha$ means that the sum over pairs of nearest neighbors is restricted to those for which \mathbf{r}_{ij} is along an α axis. It should be clear that \mathcal{H}_{KK} will inherit whatever symmetries which are present in \mathcal{H}_H , although additional symmetries are to be expected. For instance, one can regard the elimination of states in which any site is doubly occupied as resulting from a canonical transformation which eliminates such states.²⁰ Such a program can be carried out for the single-band Hubbard model, even when it is not at half filling.²¹ The important point is that whatever rotational symmetries we uncover in \mathcal{H}_H should apply also to \mathcal{H}_{KK} . On the other hand, the conservation law that each site has a single

electron will only hold for \mathcal{H}_{KK} because it is precisely the double-occupancy sites which have been eliminated by the canonical transformation.

III. HIDDEN ROTATIONAL SYMMETRY

Previously in I (Ref. 16) we pointed out several unusual symmetries of the effective Hamiltonian \mathcal{H}_{KK} . Here we extend our analysis to the underlying Hubbard model. It is useful to rewrite \mathcal{H}_H to display explicitly the form of the hopping matrix element:

$$\begin{aligned} \mathcal{H}_H = & \sum_{i\alpha\sigma} \tilde{\epsilon}_\alpha N_\alpha(i) + t \sum_{ij}' \sum_{\alpha \neq ij} \sum_{\sigma} c_{i\alpha\sigma}^\dagger c_{j\alpha\sigma} \\ & + \frac{1}{2} \sum_i \sum_{\alpha\beta} U_{\alpha\beta} N_\alpha(i) N_\beta(i), \end{aligned} \quad (5)$$

where the prime on the sum over i and j limits this sum to the case when these sites are nearest neighbors of one another.

First we show that the total number of electrons in α orbitals in any chosen plane of sites perpendicular to the α axis is conserved. For that purpose we note that the only operator which changes the occupancy of orbital states is the hopping term \mathbf{T} , where

$$\mathbf{T} = t \sum_{ij}' \sum_{\alpha \neq ij} \sum_{\sigma} c_{i\alpha\sigma}^\dagger c_{j\alpha\sigma}. \quad (6)$$

Electrons in an α orbital may hop only to another α orbital. Thus, the total number of α electrons (by this we mean electrons in α orbitals) is a good quantum number.¹⁹ Furthermore, hopping between α orbitals can only take place within the same α plane—i.e., within the same plane perpendicular to the α axis, which is the inactive axis for α -flavor electrons. Thus, the total number of α electrons in each α plane is a good quantum number, so that the operator $N_\alpha(\alpha_0)$ commutes with the Hamiltonian, where

$$N_\alpha(\alpha_0) \equiv \sum_{i \in \alpha_0} \sum_{\sigma} c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma}. \quad (7)$$

Here the notation $i \in \alpha_0$ indicates that i is summed over all sites in the α plane for which $r_{i\alpha} = \alpha_0$, where $r_{i\alpha}$ is the α component of the position of site i . As mentioned, this property must be inherited by the KK Hamiltonian, and indeed one can show this explicitly.¹⁶

We now consider the much more general symmetry induced by an arbitrary unitary transformation among spin states of a given orbital flavor. We consider the effect of the transformation applied to operators on site i ,

$$c_{i\alpha\sigma}^\dagger = \sum_{\eta} \mathbf{U}_{\sigma\eta} \tilde{c}_{i\alpha\eta}^\dagger \quad (8)$$

and

$$c_{i\alpha\sigma} = \sum_{\eta} \mathbf{U}_{\sigma\eta}^* \tilde{c}_{i\alpha\eta} = \sum_{\eta} \mathbf{U}_{\eta\sigma}^\dagger \tilde{c}_{i\alpha\eta}, \quad (9)$$

where \mathbf{U} is an arbitrary two-dimensional unitary matrix and α is a fixed flavor, the choice of which is arbitrary. Note that

$$\begin{aligned} N_\alpha(i) &= \sum_\sigma c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma} = \sum_{\sigma\eta\rho} \mathbf{U}_{\sigma\eta} \mathbf{U}_{\rho\sigma}^\dagger \tilde{c}_{i\alpha\eta}^\dagger \tilde{c}_{i\alpha\rho} \\ &= \sum_{\eta\rho} [\mathbf{U}^\dagger \mathbf{U}]_{\rho\eta} \tilde{c}_{i\alpha\eta}^\dagger \tilde{c}_{i\alpha\rho} \\ &= \sum_\eta \tilde{c}_{i\alpha\eta}^\dagger \tilde{c}_{i\alpha\eta} = \tilde{N}_\alpha(i). \end{aligned} \quad (10)$$

This shows that the first and third terms of Eq. (5) are invariant under this type of local unitary transformation applied only to orbital α on site i . The second term will likewise be invariant under an arbitrary \mathbf{U}_2 transformation, providing we transform all operators connected by hopping in the same way. This means that we set

$$c_{i\beta\sigma}^\dagger = \sum_\eta \mathbf{U}_{\sigma\eta}(i, \beta) \tilde{c}_{i\beta\eta}^\dagger \quad (11)$$

and

$$c_{i\beta\sigma} = \sum_\eta \mathbf{U}_{\eta\sigma}^\dagger(i, \beta) \tilde{c}_{i\beta\eta}, \quad (12)$$

where $\mathbf{U}(i, \beta)$ is the unit (2×2) matrix, unless both $\beta = \alpha$ and i is in the given α plane, $r_{i\alpha} = \alpha_0$, in which case $\mathbf{U}(i, \beta) = \mathbf{U}$, where \mathbf{U} is an arbitrary two-dimensional unitary matrix. Thus we apply the transformation \mathbf{U} to all electrons of a given orbital flavor *which are in an arbitrarily chosen plane perpendicular to the inactive axis for this flavor*. To see what this means, we write the spin operator for α -electrons in the chosen plane as

$$\mathbf{S}_\alpha(\alpha_0) = \sum_{r_{i\alpha}=\alpha_0} \sum_{\eta\sigma} c_{i\alpha\sigma}^\dagger \boldsymbol{\sigma}_{\sigma\eta} c_{i\alpha\eta} \equiv \sum_{r_{i\alpha}=\alpha_0} \mathbf{S}_{i\alpha}, \quad (13)$$

where $\mathbf{S}_{i\alpha}$ is the vector spin operator for electrons on site i of orbital flavor α . Then we conclude that since \mathbf{U} is an arbitrarily chosen unitary matrix, the above discussion shows that $\mathbf{S}_\alpha(\alpha_0)$, the total spin summed over all electrons in orbital α which are in any arbitrarily chosen α plane, can be rotated arbitrarily at zero cost in energy. In other words the total spin of this orbital flavor in an arbitrarily chosen plane perpendicular to the inactive axis of this flavor, as well as the z component of this total spin, is also a good quantum number. Applying the transformation (11) and (12) to the KK Hamiltonian (4) we note that, as should be the case, this Hamiltonian is also invariant under the rotation of the total spin of all electrons in orbital α in a given α plane.

We now discuss these results. First of all, the KK Hamiltonian of Eq. (2) is somewhat similar to the Heisenberg Hamiltonian in that it involves the scalar product of spin operators on different sites. This form guarantees that the Hamiltonian is invariant under a global rotation of spin. We have demonstrated a much stronger symmetry, which only holds because the constant added to $\sigma_i \cdot \sigma_j$ in Eq. (2) is unity. [Only in this case is it possible to write Eq. (4) in the alter-

nate form of Eq. (2).] Furthermore, had we allowed Coulomb exchange in the Hubbard Hamiltonian; that is, had we allowed spin exchange in the Coulomb interaction term of Eq. (5), then we would have global spin rotation (just as in the Heisenberg case), but we would not have had the invariance against independent rotations of the spins of each flavor. In fact, any interaction which allows an electron of one orbital flavor to convert (via hopping or some other interaction) into a different orbital flavor will also clearly invalidate the property that allows independent spin rotations for different orbital flavors. Probably the most important perturbation which allows such off-diagonal hopping in orbital flavor is the non-collinear M -O- M bonding due to the rotation of the MO_6 octahedra in real transition-metal oxides. This rotation angle is 156° in LaTiO_3 (Ref. 12) and therefore it has to be taken into account in any theory to explain the observed experimental properties of LaTiO_3 . Similarly, this symmetry is also destroyed by spin-orbit interactions, Coulomb exchange interactions, hopping between second nearest-neighbor oxygen ions, and less importantly by direct exchange between nearest-neighbor Ti ions and by dipolar interactions.

IV. MERMIN-WAGNER CONSTRUCTION

In I we used a Mermin-Wagner construction²² to establish the absence of long-range spin order due to the KK Hamiltonian in three (or fewer) dimensions, but we did not give full details of this construction. Here we present such a construction, but obtain a more powerful result by working with the Hubbard Hamiltonian. Results obtained from the KK Hamiltonian are only valid to leading order in t/U . By working with the Hubbard model Hamiltonian, we will establish these results to all orders in t/U for the Hamiltonian of Eq. (5).

The Mermin-Wagner construction relies on the Bogoliubov inequality,²³ which is

$$\frac{1}{2} \langle [[C, \mathcal{H}]_-, C^\dagger]_- \rangle \langle \{A, A^\dagger\}_+ \rangle \geq kT |\langle [C, A]_- \rangle|^2, \quad (14)$$

where $\langle X \rangle$ denotes the canonical average of the operator X at temperature T , $[X, Y]_-$ is the commutator of X and Y , and $\{X, Y\}_+$ is the anticommutator of X and Y . As we shall see, it is also crucial to note that

$$C_{\mathcal{H}} \equiv \langle [[C, \mathcal{H}]_-, C^\dagger]_- \rangle > 0, \quad (15)$$

unless $[C, \mathcal{H}]_- = 0$, in which $C_{\mathcal{H}} = 0$. To verify this we write out the expression for $C_{\mathcal{H}}$ in terms of the system's exact energy eigenstates, $|n\rangle$:

$$\begin{aligned} C_{\mathcal{H}} &= \sum_{n,m} p_n [\langle n|C|m\rangle (E_m - E_n) \langle m|C^\dagger|n\rangle - \langle n|C^\dagger|m\rangle \\ &\quad \times \langle m|C|n\rangle (E_n - E_m)], \end{aligned} \quad (16)$$

with $p_n = e^{-\beta E_n}/Z$, where Z is the partition function,

$$Z = \sum_n e^{-\beta E_n}, \quad (17)$$

and $\beta = 1/(kT)$. In the second term of Eq. (16) we interchange the roles of n and m , after which we obtain

$$C_{\mathcal{H}} = \sum_{n,m} |\langle n|C|m\rangle|^2 [p_n - p_m][E_m - E_n]. \quad (18)$$

We have that

$$\begin{aligned} & [p_n - p_m][E_m - E_n] \\ &= Z^{-1} e^{-\beta(E_n + E_m)/2} \{2E_{n,m} \sinh[(\beta E_{n,m}/2)]\}, \end{aligned} \quad (19)$$

where $E_{n,m} = E_n - E_m$. Thus the summand in Eq. (18) is non-negative. In fact, for $C_{\mathcal{H}}$ to be zero, one has to have $\langle n|C|m\rangle = 0$ whenever $E_n \neq E_m$. In other words, $C_{\mathcal{H}}$ is real and non-negative and can only be zero if the operator C commutes with the Hamiltonian, a case we will not encounter here.

For the purposes of this construction we will add to the Hamiltonian a term conjugate to the magnetization at wave vector \mathbf{K} of electrons in α orbitals, so that we treat the Hamiltonian

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_H - \frac{1}{2} h \sum_{\mathbf{R}} e^{i\mathbf{K} \cdot \mathbf{R}} [c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\uparrow} - c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\downarrow}] \\ &\equiv \mathcal{H}_H - h \sum_{\mathbf{R}} e^{i\mathbf{K} \cdot \mathbf{R}} S_{\mathbf{R}\alpha}^z \\ &\equiv \mathcal{H}_H - h N S_{\mathbf{K}\alpha}^z, \end{aligned} \quad (20)$$

where $\mathbf{S}_{\mathbf{R}\alpha}$ is the spin operator for the α orbital of site \mathbf{R} , as in Eq. (13). We will set the order-parameter wave vector \mathbf{K} to be zero to exclude ferromagnetic long-range order and to be $(\pi, \pi, \pi)/a$ to exclude antiferromagnetic long-range order, where a is the lattice constant. However, as can be seen later, we may choose \mathbf{K} arbitrarily, in which case our construction excludes the possibility of long-range order at whatever \mathbf{K} is chosen.

To rule out long-range spin ordering, we apply Eq. (14), taking

$$C_{\mathbf{k}} = \sum_{\mathbf{R}} e^{-i\mathbf{k} \cdot \mathbf{R}} c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}, \quad (21)$$

$$A_{\mathbf{k}} = \sum_{\mathbf{R}} e^{i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{R}} c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\uparrow}, \quad (22)$$

where \mathbf{R} is a lattice site. Note that the operator $c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}$ can be identified as $S_{\mathbf{R}\alpha}^+$, the raising operator for $\mathbf{S}_{\mathbf{R}\alpha}$. Then Eq. (14) gives

$$\sum_{\mathbf{k}} \langle \{A_{\mathbf{k}}, A_{\mathbf{k}}^\dagger\}_+ \rangle \geq 2kT \sum_{\mathbf{k}} \frac{|\langle [C_{\mathbf{k}}, A_{\mathbf{k}}]_- \rangle|^2}{\langle [[C_{\mathbf{k}}, \mathcal{H}]_-, C_{\mathbf{k}}^\dagger]_- \rangle}. \quad (23)$$

Here and below the sum over \mathbf{k} is over the N wave vectors of the first Brillouin zone, where N is the total number of sites. We have

$$\begin{aligned} \sum_{\mathbf{k}} \langle \{A_{\mathbf{k}}, A_{\mathbf{k}}^\dagger\}_+ \rangle &= \sum_{\mathbf{k}} \sum_{\mathbf{R}} \sum_{\mathbf{S}} e^{i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{R}} e^{-i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{S}} \\ &\quad \times \langle \{c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\uparrow}, c_{\mathbf{S}\alpha\uparrow}^\dagger c_{\mathbf{S}\alpha\downarrow}\}_+ \rangle. \end{aligned} \quad (24)$$

The sum over \mathbf{k} gives $N \delta_{\mathbf{R}, \mathbf{S}}$, so that

$$\sum_{\mathbf{k}} \langle \{A_{\mathbf{k}}, A_{\mathbf{k}}^\dagger\}_+ \rangle = N \sum_{\mathbf{R}} \langle \{c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\uparrow}, c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}\}_+ \rangle. \quad (25)$$

Here the sum over \mathbf{R} consists of a sum of $2N$ products, each of which is bounded by unity. Thus we have

$$2N^2 \geq \sum_{\mathbf{k}} \langle \{A_{\mathbf{k}}, A_{\mathbf{k}}^\dagger\}_+ \rangle, \quad (26)$$

which gives

$$N^2 \geq kT \sum_{\mathbf{k}} \frac{|\langle [C_{\mathbf{k}}, A_{\mathbf{k}}]_- \rangle|^2}{\langle [[C_{\mathbf{k}}, \mathcal{H}]_-, C_{\mathbf{k}}^\dagger]_- \rangle}. \quad (27)$$

Now we evaluate

$$\begin{aligned} [C_{\mathbf{k}}, A_{\mathbf{k}}]_- &= \sum_{\mathbf{R}, \mathbf{S}} e^{-i\mathbf{k} \cdot \mathbf{R}} e^{i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{S}} [c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}, c_{\mathbf{S}\alpha\downarrow}^\dagger c_{\mathbf{S}\alpha\uparrow}]_- \\ &= \sum_{\mathbf{R}} e^{i\mathbf{K} \cdot \mathbf{R}} [c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}, c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\uparrow}]_- . \end{aligned} \quad (28)$$

Using

$$\begin{aligned} [AB, CD]_- &= A\{B, C\}_+ D - \{A, C\}_+ BD + CA\{B, D\}_+ \\ &\quad - C\{A, D\}_+ B, \end{aligned} \quad (29)$$

we then get

$$[c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}, c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\uparrow}]_- = c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\uparrow} - c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\downarrow} \quad (30)$$

(which is nothing more than $[S_{\mathbf{R}\alpha}^+, S_{\mathbf{R}\alpha}^-]_- = 2S_{\mathbf{R}\alpha}^z$), so that

$$\langle [C_{\mathbf{k}}, A_{\mathbf{k}}]_- \rangle = 2 \sum_{\mathbf{R}} e^{i\mathbf{K} \cdot \mathbf{R}} S_{\mathbf{R}\alpha}^z = 2N S_{\mathbf{K}\alpha}^z. \quad (31)$$

For $K=0$ $S_{\mathbf{K}\alpha}^z$ is the z component of the spin per site of α -flavor orbitals and for $\mathbf{K} = (\pi, \pi, \pi)/a$ it is the z component of the staggered magnetization per site of α -flavor orbitals. (For general \mathbf{K} it is the amplitude of the Fourier component of the z component of spin of α -flavor orbitals at wave vector \mathbf{K} .) We concentrate on the ferromagnetic and antiferromagnetic cases. We have the inequality

$$1 \geq 4kT |S_{\mathbf{K}\alpha}^z|^2 \sum_{\mathbf{k}} \langle X_{\mathbf{k}} \rangle^{-1}, \quad (32)$$

where $X_{\mathbf{k}}$ is positive real and is given by

$$X_{\mathbf{k}} = [[C_{\mathbf{k}}, \mathcal{H}]_-, C_{\mathbf{k}}^\dagger]_- . \quad (33)$$

Now we need the double commutator of $C_{\mathbf{k}}$ with \mathcal{H} . The Hamiltonian is the sum of four terms: T_1 involving the hopping matrix element t_{ij}^α , T_2 involving the crystal field energies ϵ_α , T_3 the on-site Coulomb interaction, and T_4 the interaction with the staggered field $h > 0$. Since T_2 and T_3 depend only on $N_\alpha(i)$, one can establish that

$$[C_{\mathbf{k}}, T_2]_- = [C_{\mathbf{k}}, T_3]_- = 0. \quad (34)$$

Also

$$[C_{\mathbf{k}}, T_4]_- = h \sum_{\mathbf{R}} e^{i(\mathbf{K}-\mathbf{k}) \cdot \mathbf{R}} c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}, \quad (35)$$

so that

$$\begin{aligned} \langle [[C_{\mathbf{k}}, T_4]_-, C_{\mathbf{k}}^\dagger]_- \rangle &= \left\langle h \sum_{\mathbf{R}} e^{i\mathbf{K} \cdot \mathbf{R}} [c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}, c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\uparrow}]_- \right\rangle \\ &= h \sum_{\mathbf{R}} e^{i\mathbf{K} \cdot \mathbf{R}} \langle [c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\uparrow} - c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\downarrow}] \rangle \\ &= 2NhS_{\mathbf{K}\alpha}^z. \end{aligned} \quad (36)$$

The crucial calculation is the commutator involving T_1 :

$$\begin{aligned} Y_{\mathbf{k}} &\equiv [C_{\mathbf{k}}, T_1]_- \\ &= \sum_{\mathbf{R}} e^{-i\mathbf{k} \cdot \mathbf{R}} \left[c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}, \sum_{\mathbf{S}, \mathbf{T}, \sigma} t_\alpha(\mathbf{S}, \mathbf{T}) c_{\mathbf{S}\alpha\sigma}^\dagger c_{\mathbf{T}\alpha\sigma} \right]_-, \end{aligned} \quad (37)$$

where \mathbf{R} , \mathbf{S} , and \mathbf{T} are lattice sites and we dropped terms involving orbitals other than α since they obviously commute with $C_{\mathbf{k}}$. Also in this section we set $t_\alpha(\mathbf{R}, \mathbf{S}) = t_\alpha(\mathbf{R} - \mathbf{S})$ to denote the hopping matrix element (assumed to be nonnegative for convenience) between α orbitals on sites \mathbf{R} and \mathbf{S} and we use $t_\alpha(\mathbf{R}) = t_\alpha(-\mathbf{R})$.

We have

$$\begin{aligned} Y_{\mathbf{k}} &= \sum_{\mathbf{R}, \mathbf{S}, \mathbf{T}, \sigma} e^{-i\mathbf{k} \cdot \mathbf{R}} t_\alpha(\mathbf{S}, \mathbf{T}) [c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\downarrow}, c_{\mathbf{S}\alpha\sigma}^\dagger c_{\mathbf{T}\alpha\sigma}]_- \\ &= \sum_{\mathbf{R}, \mathbf{S}, \mathbf{T}} e^{-i\mathbf{k} \cdot \mathbf{R}} t_\alpha(\mathbf{S}, \mathbf{T}) [c_{\mathbf{R}\alpha\uparrow}^\dagger \delta_{\mathbf{R}, \mathbf{S}} c_{\mathbf{T}\alpha\downarrow} - c_{\mathbf{S}\alpha\uparrow}^\dagger \delta_{\mathbf{R}, \mathbf{T}} c_{\mathbf{R}\alpha\downarrow}] \\ &= \sum_{\mathbf{R}, \delta} e^{-i\mathbf{k} \cdot \mathbf{R}} t_\alpha(\delta) [1 - e^{-i\mathbf{k} \cdot \delta}] c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}+\delta\alpha\downarrow}, \end{aligned} \quad (38)$$

where δ is a nearest-neighbor vector. Then

$$\begin{aligned} X_{\mathbf{k}} &\equiv [[C_{\mathbf{k}}, T_1]_-, C_{\mathbf{k}}^\dagger]_- + 2NhS_{\mathbf{K}\alpha}^z \\ &= [Y_{\mathbf{k}}, C_{\mathbf{k}}^\dagger]_- + 2NhS_{\mathbf{K}\alpha}^z \\ &= \sum_{\mathbf{R}, \delta} e^{i\mathbf{k} \cdot (\mathbf{S}-\mathbf{R})} t_\alpha(\delta) [1 - e^{-i\mathbf{k} \cdot \delta}] \\ &\quad \times [c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}+\delta\alpha\downarrow}, c_{\mathbf{S}\alpha\downarrow}^\dagger c_{\mathbf{S}\alpha\uparrow}]_- + 2NhS_{\mathbf{K}\alpha}^z \end{aligned}$$

$$\begin{aligned} &= \sum_{\mathbf{R}, \delta} t_\alpha(\delta) [1 - e^{-i\mathbf{k} \cdot \delta}] [e^{i\mathbf{k} \cdot \delta} c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}+\delta\alpha\uparrow} - c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}+\delta\alpha\downarrow}] \\ &\quad + 2NhS_{\mathbf{K}\alpha}^z \\ &= \sum_{\mathbf{R}, \delta} t_\alpha(\delta) [(e^{i\mathbf{k} \cdot \delta} - 1) c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}+\delta\alpha\uparrow} \\ &\quad + (e^{-i\mathbf{k} \cdot \delta} - 1) c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}+\delta\alpha\downarrow}] + 2NhS_{\mathbf{K}\alpha}^z. \end{aligned} \quad (39)$$

According to Eq. (15) the quantity $\langle X_{\mathbf{k}} \rangle$ is real and positive (no matter what the value of \mathbf{k}) and therefore we can maintain the inequality (32) if we replace the sum \mathcal{S} , where

$$\mathcal{S} \equiv \sum_{\mathbf{k}} \frac{1}{\langle X_{\mathbf{k}} \rangle}, \quad (40)$$

by a quantity which is less than \mathcal{S} . To do that we write

$$\mathcal{S} \equiv \sum_{\mathbf{k}} \frac{1}{2} \left(\frac{1}{\langle X_{\mathbf{k}} \rangle} + \frac{1}{\langle X_{-\mathbf{k}} \rangle} \right) \geq \sum_{\mathbf{k}} \frac{2}{\langle X_{\mathbf{k}} \rangle + \langle X_{-\mathbf{k}} \rangle}. \quad (41)$$

This follows from the fact that when a and b are positive, then $a^{-1} + b^{-1} \geq 4/(a+b)$. Thus

$$1 \geq 8kT |S_{\mathbf{K}\alpha}^z|^2 \sum_{\mathbf{k}} [\langle X_{\mathbf{k}} \rangle + \langle X_{-\mathbf{k}} \rangle]^{-1}. \quad (42)$$

Here

$$\begin{aligned} [\langle X_{\mathbf{k}} \rangle + \langle X_{-\mathbf{k}} \rangle] / 2 &= \sum_{\mathbf{R}, \delta} t_\alpha(\delta) [\cos(\mathbf{k} \cdot \delta) - 1] \langle c_{\mathbf{R}\alpha\uparrow}^\dagger c_{\mathbf{R}+\delta\alpha\uparrow} \\ &\quad + c_{\mathbf{R}\alpha\downarrow}^\dagger c_{\mathbf{R}+\delta\alpha\downarrow} \rangle + 2NhS_{\mathbf{K}\alpha}^z. \end{aligned} \quad (43)$$

Since the quantity on the right-hand side of Eq. (43) is positive, we may replace it (without increasing \mathcal{S}) by the sum of the absolute values of bounds to its terms, so that finally Eq. (42) yields

$$\begin{aligned} 4kT |S_{\mathbf{K}\alpha}^z|^2 &\leq \left[\frac{1}{N} \sum_{\mathbf{k}} \left(\sum_{\delta} t_\alpha(\delta) [1 - \cos(\mathbf{k} \cdot \delta)] \right. \right. \\ &\quad \left. \left. + |h| |S_{\mathbf{K}\alpha}^z| \right)^{-1} \right]^{-1} = t/I, \end{aligned} \quad (44)$$

where

$$I = \frac{t}{N} \sum_{\mathbf{k}} \left(\sum_{\delta} t_\alpha(\delta) [1 - \cos(\mathbf{k} \cdot \delta)] + |h| |S_{\mathbf{K}\alpha}^z| \right)^{-1} \quad (45)$$

and we have used the bound

$$|\langle c_{\mathbf{R}+\delta\alpha\uparrow}^\dagger c_{\mathbf{R}\alpha\uparrow} \rangle + \langle c_{\mathbf{R}+\delta\alpha\downarrow}^\dagger c_{\mathbf{R}\alpha\downarrow} \rangle| \leq 2C_0, \quad (46)$$

where $C_0 = 1$. In I we gave the result obtained in an entirely analogous fashion from the KK Hamiltonian. That result is valid for the KK Hamiltonian, which itself assumes the validity of the expansion in powers of t/U . That result could be obtained here by noting that to lowest order in perturbation theory in t/U , the left-hand side of Eq. (46) is given by²⁴ $C_0 \sim 2|t/U|$. The present result avoids any rigorous discus-

sion of the validity of the expansion in powers of t/U , but uses the much cruder bound of Eq. (46) with $C_0=1$. In any event, an entirely analogous construction can be carried out for the KK Hamiltonian, as discussed in I.

The analysis can now be less formal. We estimate the quantity I on the right-hand side of Eq. (45). For $\alpha=z$, for example, we have

$$\sum_{\delta} t_{\alpha}(\delta)[1 - \cos(\mathbf{k} \cdot \delta)] = 2t[2 - \cos(k_x a) - \cos(k_y a)]. \quad (47)$$

Since the sum over \mathbf{k} is dominated by small $|\mathbf{k}|$, we may write

$$I = A \int_0^{x_0} \frac{2k_{\perp} dk_{\perp}}{k_{\perp}^2 + B|h||S_{\mathbf{k}_z}^z|/t} = A \ln \left[1 + \frac{tx_0^2}{B|h||S_{\mathbf{k}_z}^z|} \right], \quad (48)$$

where A , B , and x_0 are constants of order unity, whose exact values need not concern us. In all we obtain the bound

$$|S_{\mathbf{k}_z}^z| \leq A' T^{-1/2} |\ln|h|/t|^{-1/2}, \quad (49)$$

where A' is a constant. Obviously, this bound applies also to any of the other components $S_{\mathbf{k}_\alpha}^\mu$ of the spin of any flavor α . This bound implies that as $h \rightarrow 0$, we must have $|S_{\mathbf{k}_\alpha}^\mu| \rightarrow 0$, for all choices of \mathbf{K} , α , and μ . Thus we conclude that this Hubbard model (and perforce also the KK Hamiltonian obtained from it) cannot support spontaneous long-range spin order at any nonzero temperature. Our rigorous arguments have nothing to say about orbital order. However, we believe that there is no spontaneous long-range orbital order for the KK model with no spin-orbit interactions.

From the form of the bound we also expect that the lower critical dimension for the appearance of long-range spin order is $d_c = 3$. As will be discussed elsewhere,²⁵ this conclusion can also be understood within a renormalization group analysis.

The above development allows us to make some comments on whether or not there can be spontaneous breaking of parity symmetry. Note that the average of the quantity on the right-hand side of Eq. (39) must be positive. However, apart from the term proportional to h , this quantity vanishes for $\mathbf{k}=0$ and has a term linear in \mathbf{k} . The term linear in \mathbf{k} gives a contribution to $\langle X_{\mathbf{k}} \rangle$ of

$$\delta \langle X_{\mathbf{k}} \rangle = i \sum_{\mathbf{R}\delta} t_{\alpha}(\delta)(\mathbf{k} \cdot \delta) \langle c_{\mathbf{R}\alpha\uparrow}^{\dagger} c_{\mathbf{R}+\delta\alpha\uparrow} - c_{\mathbf{R}\alpha\downarrow}^{\dagger} c_{\mathbf{R}+\delta\alpha\downarrow} \rangle. \quad (50)$$

This quantity must be real, but must also go to zero as $h \rightarrow 0$, in order that $\langle X_{\mathbf{k}} \rangle$ always be positive. If parity is preserved, then, of course, $\langle c_{\mathbf{R}\alpha\sigma}^{\dagger} c_{\mathbf{R}+\delta\alpha\sigma} \rangle = \langle c_{\mathbf{R}\alpha\sigma}^{\dagger} c_{\mathbf{R}-\delta\alpha\sigma} \rangle$ and the term linear in \mathbf{k} does vanish. The converse is not quite proved because the quantity in Eq. (50) could vanish without parity being maintained. So this development rules out a spin-independent breaking of parity. In addition, we remind the reader that we can choose \mathbf{K} arbitrarily, after which the above argument rules out spontaneous helical spin order.

V. EXACT DIAGONALIZATION

In this section we show that the hidden symmetries discussed above are very useful in simplifying the exact numerical studies of small clusters. Such cluster studies are very important, because they provide a way of checking analytical results and also give insight into the nature of the ground state when there is no long-range order. The main problem in such studies of finite clusters is usually the large matrix sizes that have to be diagonalized. For example, to treat the KK Hamiltonian for a cube of eight sites requires the diagonalization of a matrix of dimensionality $6^8 \approx 1.7 \times 10^6$. Since the KK Hamiltonian is rotationally invariant, one can obtain the full spectrum by working within the subspace of $\sum_{i=1}^8 S_i^z = 0$, where the size of the Hamiltonian matrix is now reduced to $70 \times 3^8 \approx 1/2 \times 10^6$. The spin degeneracy of each individual state in this manifold is $2S+1$, where $S(S+1)$ is the square of the total spin of the wave function.

Initially we obtained the low-energy spectrum of eigenstates for a cube of eight Ti ions by diagonalizing the $1/2 \times 10^6$ dimensional matrix described above. Since the Hamiltonian matrix is very sparse, it is possible to obtain the eigenvalues and the corresponding eigenvectors in a small interval of the spectrum starting from the lowest eigenvalue, using a standard sparse matrix diagonalization routine. The ground state is found to be threefold degenerate, with energy -6.2716ϵ . By analyzing the wave functions we found that the ground state had a total spin $S=0$ and either $N_x=4$, $N_y=4$, $N_z=0$, or the two cyclic permutations of these quantum numbers, where N_{α} is the total number of α -flavor electrons.

The same energy spectrum and the corresponding wave functions can also be found by diagonalizing much smaller matrices if one works within a manifold defined by the conserved numbers applied to each face of the cube (see Fig. 3). We actually have 18 conserved quantum numbers and there is an astonishing numerical simplification when maximal use is made of these symmetries. For example, the ground state found by dealing with the matrix of dimensionality $1/2 \times 10^6$ could alternatively be found by diagonalizing the Hamiltonian matrix within a manifold of just 16 states. Given the fact that the ground state has $S=0$ and $N_x=N_y=4$, one can easily conclude that this corresponds to having $N_{x,1}=2$ electrons in x orbitals in the first x plane and $N_{x,2}=2$ electrons in x orbitals in the second x plane. For any asymmetric choice, such as $N_{x,1}=1$ and $N_{x,2}=3$, for instance, one would have an additional degeneracy associated with interchanging $N_{x,1}$ and $N_{x,2}$. Thus we were sure that these states found numerically had to have the quantum numbers $N_{x,1}=N_{x,2}=N_{y,1}=N_{y,2}=2$. In addition, the total spin of the two x electrons in each x plane had to be zero in order to be consistent with the lack of spin degeneracy. Thus it was clear that the ground state had to consist of a sum of terms, each term being a product of four spin singlets. We define

$$|(ij)_x\rangle \equiv 2^{-1/2} [c_{ix\uparrow}^{\dagger} c_{jx\downarrow}^{\dagger} - c_{ix\downarrow}^{\dagger} c_{jx\uparrow}^{\dagger}] |\text{vac}\rangle = |(ji)_x\rangle, \quad (51)$$

with a similar definition of $(ij)_y$, where $|\text{vac}\rangle$ is the vacuum state. Then the ground state consists of a linear combination

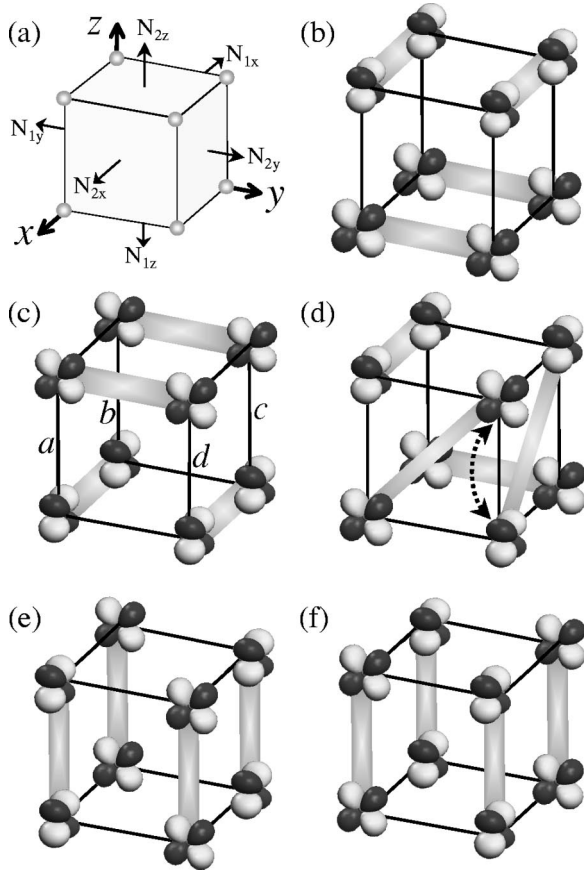


FIG. 3. Spin and orbital configurations for a cube of eight sites. The thick lines indicate singlet spin states (dimers) and X and Y indicate the orbital states of the electrons. (a) Schematic illustration of the quantum numbers associated with occupation of α orbitals in an α plane. (Similar spin quantum numbers are not shown.) (b) and (c) Dominant configurations in the ground-state wave function. Hopping between x and y orbital states is only allowed along z -direction bonds and these bonds are labeled in panel (c). (d) A subdominant configuration in the ground state which is obtained from (b) by allowing the interchange of two (X and Y) electrons along the z -axis bond labeled “d” while each electron retains its membership in its original spin singlets (even though the position of the electron has changed). If $|0\rangle$ denotes configuration (c), then configuration (b) is $|\bar{0}\rangle \equiv abcd|0\rangle$ and (d) is $d|0\rangle$ in the notation of Table I. We also show (e) and (f) states with the same quantum numbers but which are not coupled to the manifold of 16 states we analyze. These two states are actually eigenstates of the Hamiltonian with energy -4ϵ .

of terms, each term being a product of four dimer singlets which we write as

$$|(ij)_x(kl)_x(mn)_y(op)_y\rangle, \quad (52)$$

where the sites i and j are in the first x plane, k and l are in the second x plane, m and n are in the first y plane, and o and p are in the second y plane. The dominant configurations in the ground state are the dimer states with the lowest expectation value of the Hamiltonian: namely, the states in panels (b) and (c) of Fig. 3. From one of these—say, the one shown in panel (c)—one can generate the manifold of states which

can be obtained by hopping along one or more of the z -directed bonds, labeled a , b , c , and d in the figure. The Hamiltonian matrix within this manifold of 16 states is given explicitly in Table I.²⁶ To construct this matrix we used the fact that

$$\langle (ij)_\alpha | \mathcal{H}_{\text{KK}} | (ij)_\alpha \rangle \quad (53)$$

is $-\epsilon$ if sites i and j are NN’s along an axis which is *not* inactive for α orbitals. Otherwise this matrix element is zero. [For instance, diagonal dimers like the X and Y dimers involved in the hopping shown in panel (d) of Fig. 3 make zero contribution to the diagonal matrix element. So configuration (d) has a diagonal matrix element of -2ϵ due to the NN X and Y dimers.] Also the matrix element

$$\langle (ij)_x(mn)_y | \mathcal{H} | (mj)_x(in)_y \rangle \quad (54)$$

has the value $-\epsilon$ if the sites i and m which are involved in the hopping are NN’s along the active (z) direction and is zero otherwise. It is amazing to us that the original Hamiltonian, which was obtained from a matrix of dimensionality approximately $1/2 \times 10^6$, could be reduced by symmetry considerations to an eigenvalue problem of dimension 16. The existence of these symmetries was numerically confirmed when we found the same value for the ground-state energy from the 16-dimensional matrix as from the full matrix. The ground-state wave function, in terms of the states in the order used for the matrix, is

$$(\alpha, \beta, \beta, \beta, \beta, \gamma, \gamma, \delta, \delta, \gamma, \gamma, \beta, \beta, \beta, \alpha), \quad (55)$$

where $\alpha = 0.409\,15$, $\beta = 0.232\,35$, $\gamma = 0.217\,58$, and $\delta = 0.148\,19$, with an uncertainty in the last digit quoted.

VI. SYMMETRY, SPIN-ORBIT INTERACTION, AND THE EXCITATION SPECTRUM

Here we consider the addition of a perturbation which breaks the symmetry whereby each orbital flavor of spin can independently be rotated at zero cost in energy. For concreteness we consider the spin-orbit interaction. Possibly one’s first intuition about the effect of the spin-orbit interaction would be that it would cause the system to exhibit long-range order (this is correct) and that the elementary excitation spectrum would have a gap, because the orbits would define a set of favored directions. In a study of a similar Hubbard model for the cuprates this second conclusion was shown to be false.⁸ In fact, there it was shown that the addition of spin-orbit interactions to an isotropic Hubbard model did *not* lead to a gap in the spin-wave spectrum, but that a gap does result with the addition of both spin-orbit and Coulomb exchange interactions (these are sometimes called Hund’s rule coupling). Here we will establish the first part of this scenario: namely, that adding only spin-orbit interactions to the KK Hamiltonian or to the Hubbard model of Eq. (1) does *not* lead to a gap in the excitation spectrum.

Following Ref. 8 we now introduce a transformation to pseudospin which yields a rotationally invariant Hamiltonian. We write²⁷

TABLE I. Hamiltonian matrix for the ground manifold in units of ϵ . The states are specified by hops relative to the state $|0\rangle$ shown in Fig. 3(c). (So a indicates hopping along the z -directed bond labeled a and similarly for b , c , and d .) We introduce the notation $\bar{\alpha} \equiv abcd\alpha$.

	0	a	b	c	d	ab	bc	bd	ac	ad	cd	\bar{d}	\bar{c}	\bar{b}	\bar{a}	$\bar{0}$
0	-4	-1	-1	-1	-1	0	0	0	0	0	0	0	0	0	0	0
a	-1	-2	0	0	0	-1	0	0	-1	-1	0	0	0	0	0	0
b	-1	0	-2	0	0	-1	-1	-1	0	0	0	0	0	0	0	0
c	-1	0	0	-2	0	0	-1	0	-1	0	-1	0	0	0	0	0
d	-1	0	0	0	-2	0	0	-1	0	-1	-1	0	0	0	0	0
ab	0	-1	-1	0	0	-2	0	0	0	0	0	-1	-1	0	0	0
bc	0	0	-1	-1	0	0	-2	0	0	0	0	-1	0	0	-1	0
bd	0	0	-1	0	-1	0	0	0	0	0	0	0	-1	0	-1	0
ac	0	-1	0	-1	0	0	0	0	0	0	0	-1	0	-1	0	0
ad	0	-1	0	0	-1	0	0	0	0	-2	0	0	-1	-1	0	0
cd	0	0	0	-1	-1	0	0	0	0	0	-2	0	0	-1	-1	0
\bar{d}	0	0	0	0	0	-1	-1	0	-1	0	0	-2	0	0	0	-1
\bar{c}	0	0	0	0	0	-1	0	-1	0	-1	0	0	-2	0	0	-1
\bar{b}	0	0	0	0	0	0	0	0	-1	-1	-1	0	0	-2	0	-1
\bar{a}	0	0	0	0	0	0	-1	-1	0	0	-1	0	0	0	-2	-1
$\bar{0}$	0	0	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-4

$$c_{i\alpha\sigma} = \sum_{\eta} [\sigma_{\alpha}]_{\sigma\eta} d_{i\alpha\eta}, \quad (56)$$

where $d_{i\alpha\eta}^{\dagger}$ creates an electron in orbital α of site i with pseudospin η . Since pseudospin is not the most intuitive concept, we will here give a discussion that avoids use of this quantity. In terms of “real” spin we will show that the Hamiltonian is invariant under the transformation

$$c_{i\alpha\sigma} = \sum_{\tau} \mathbf{V}_{\sigma\tau}^{(\alpha)} \tilde{c}_{i\alpha\tau}, \quad (57)$$

where

$$\mathbf{V}^{(\alpha)} = \sigma_{\alpha} \mathbf{U} \sigma_{\alpha}, \quad (58)$$

with an arbitrary unitary matrix \mathbf{U} .

We now consider the effect of this transformation on the Hubbard model of Eq. (1). The Coulomb interaction and single-site crystal-field energy are both clearly invariant under this transformation, because they only depend on the total number of electrons in each orbital, $\sum_{\sigma} c_{i\alpha\sigma}^{\dagger} c_{i\alpha\sigma}$, and this quantity is not changed by this transformation. Since hopping is diagonal in the orbital indices, the hopping term is also invariant under this transformation. Finally, we study how the additional spin-orbit interaction transforms. We write this interaction as

$$V_{\text{S-O}} = \lambda \sum_i \sum_{\alpha\beta\gamma} \sum_{\mu\nu} \langle \alpha | L_{\gamma} | \beta \rangle [\sigma_{\gamma}]_{\mu\nu} c_{i\alpha\mu}^{\dagger} c_{i\beta\nu}, \quad (59)$$

where $\langle \alpha | L_{\gamma} | \beta \rangle$ is the orbital angular momentum matrix element and is nonzero only when α , β , and γ are all different:

$$\langle \alpha | L_{\beta} | \gamma \rangle = -i \epsilon_{\alpha\beta\gamma}. \quad (60)$$

Thus

$$\begin{aligned} V_{\text{S-O}} &= \lambda \sum_i \sum_{\alpha\beta\gamma} \sum_{\mu\nu} \sum_{\rho\tau} \langle \alpha | L_{\gamma} | \beta \rangle \\ &\quad \times [\sigma_{\gamma}]_{\mu,\nu} [\mathbf{V}_{\mu\rho}^{(\alpha)}]^* \tilde{c}_{i\alpha\rho}^{\dagger} \mathbf{V}_{\nu\tau}^{(\beta)} \tilde{c}_{i\beta\tau} \\ &= \lambda \sum_i \sum_{\alpha\beta\gamma} \sum_{\rho\tau} \langle \alpha | L_{\gamma} | \beta \rangle \mathbf{M}_{\rho\tau} \tilde{c}_{i\alpha\rho}^{\dagger} \tilde{c}_{i\beta\tau}, \end{aligned} \quad (61)$$

where

$$\begin{aligned} \mathbf{M}_{\rho\tau} &= \sum_{\mu\nu} [\sigma_{\gamma}]_{\mu,\nu} [\mathbf{V}_{\mu\rho}^{(\alpha)}]^* \mathbf{V}_{\nu\tau}^{(\beta)} = ([\mathbf{V}^{(\alpha)}]^{\dagger} [\sigma_{\gamma}] [\mathbf{V}^{(\beta)}])_{\rho\tau} \\ &= [\sigma_{\alpha} \mathbf{U}^{\dagger} \sigma_{\alpha} \sigma_{\gamma} \sigma_{\beta} \mathbf{U} \sigma_{\beta}]_{\rho\tau}. \end{aligned} \quad (62)$$

The orbital matrix element $\langle \alpha | L_{\gamma} | \beta \rangle$ guarantees that all three of the indices α , β , and γ are different. In that case we set

$$\sigma_{\alpha} \sigma_{\gamma} \sigma_{\beta} = i \epsilon_{\alpha\gamma\beta} \mathcal{I}, \quad (63)$$

where \mathcal{I} is the unit matrix and $\epsilon_{\alpha\beta\gamma}$ is the antisymmetric tensor. Thus

$$\begin{aligned} \mathbf{M}_{\rho\tau} &= i \epsilon_{\alpha\gamma\beta} [\sigma_{\alpha} \mathbf{U}^{\dagger} \mathbf{U} \sigma_{\beta}]_{\rho\tau} = i \epsilon_{\alpha\gamma\beta} [\sigma_{\alpha} \sigma_{\beta}]_{\rho\tau} \\ &= \epsilon_{\alpha\gamma\beta}^2 [\sigma_{\gamma}]_{\rho\tau}. \end{aligned} \quad (64)$$

Since this matrix has the same form as before the transformation, we have shown that the Hubbard Hamiltonian with spin-orbit interactions is invariant against the transformation by the unitary matrix of Eq. (58), where \mathbf{U} is an arbitrary unitary matrix. Thus the invariance with respect to arbitrary rotation of pseudospin gives rise to an arbitrary transformation of real spin. This indicates that there is a continuously

degenerate manifold for the ground state, and therefore we do not expect a gap in the excitation spectrum. A rigorous analysis of the structure of the Goldstone modes is more complicated²⁸ and may require a statement of whether or not there is long-range order in the orbital sector, in order to say whether these modes are propagating or diffusive. Intuitively it seems likely that if there is long-range spin order, there should be propagating spin-wave modes, at least one of which by our argument will not have an energy gap at zero wave vector.

One final point is worth noting. We have discussed that we expect long-range antiferromagnetic spin ordering in the presence of spin-orbit coupling. Once we have antiferromagnetic spin order, the spin-orbit perturbation acts like a staggered field on the orbital variable, thus inducing long-range antiferromagnetic order in the orbital variable $\langle \mathbf{L} \rangle$. This type of orbital ordering is not the same as that in which the thermal expectation value of the orbital occupation numbers, $\langle N_\alpha \rangle$, become unequal to one another.

VII. CONCLUSIONS

In this paper we have analyzed several unusual symmetries of the three-band t_{2g} Hubbard model and the associated low-energy KK Hamiltonian for threefold-degenerate orbitals in the ideal ABO_3 cubic structure. As pointed out previously,¹⁹ it is evident that the total number of electrons in any of the three orbital states is a good quantum number. In addition,¹⁶ the number of electrons in any arbitrarily chosen plane perpendicular to the α axis which are in α orbitals is also a good quantum number. We showed that the Hamiltonian is invariant with respect to independently rotating the spins of any single orbital state α for all spins in an arbitrarily chosen plane perpendicular to the α axis (which is the inactive axis for such orbital spins). These symmetries lead to a dramatic simplification in numerical diagonalizations, as we illustrated by discussing exact diagonalizations for a cube of eight sites. Furthermore, using these symmetries we developed a rigorous Mermin-Wagner construction, which shows that the Hubbard model (and perforce the KK Hamiltonian derived from it) does not support spontaneous long-range spin order at any nonzero temperature. These unusual

symmetries are destroyed by almost any realistic perturbation. In the presence of spin-orbit coupling, for instance, we show that a special invariance with respect to the rotation of *pseudospin* remains unbroken and due to this continuous symmetry we expect the excitation spectrum to have at least one gapless Goldstone mode. In analogy with the situation in the cuprates,^{8,17} the gap one might have expected in the presence of spin-orbit interactions will only develop in the presence of both spin-orbit and Coulomb exchange interactions.²⁹

Of course, in real systems, such as LaTiO_3 , long-range spin order and a gap in the elementary excitation spectrum are observed.¹¹ However, any credible expression for T_c , for instance, must involve a perturbation beyond the isotropic “bare” KK model, because, as we have shown, this model does not support long-range spin order. Elsewhere²⁹ we discuss the type of long-range order which mean-field theory predicts when various perturbations such as (a) spin-orbit interactions, (b) NNN hopping, and (c) Hund’s rule coupling are added to the KK Hamiltonian. In addition, an important factor to consider is the distortion and/or rotation of the oxygen octahedra surrounding each Ti ion. Similarly, to be credible any theoretical expression for the gap in the excitation spectrum must involve perturbations beyond spin-orbit interactions, because we have shown that with only spin-orbit interactions added to the “bare” KK Hamiltonian, the excitation spectrum is gapless. Finally, we note that it would be very interesting to study an experimental system with as small as possible deviations from the “bare” KK model. Such a system would show quite exotic properties (such as peculiar two-dimensional correlations of spins associated with different orbital flavors).

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